UDC 666.117.2:622.349.2

LOW-MELTING GLASSES BASED ON NATURAL ALUMINOSILICATES FROM KARELIA

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Translated from Steklo i Keramika, No. 5, pp. 18 – 21, May, 2002.

The effect of the chemico-mineralogical composition of aluminosilicate rocks on the properties and structure of low-melting technical glasses is studied. Comparative studies of glasses based on traditional glass materials such as pegmatite and nepheline syenite and glasses based on nontraditional materials such as halleflinta and pure chemical reactants are performed. It has been established that the use of various natural aluminosilicate in technical glasses does not significantly disturb the glass-forming conditions but makes it necessary to adjust the ratio of the main components and additives.

The development of glass for general and special engineering purposes based on natural mineral materials is an important field of research in the contemporary glass industry. Among promising raw materials that are capable of imparting required properties and structure to glass and at the same time are available and accessible we mention aluminosilicate rocks of feldspar, quartz-feldspar, and nepheline-feldspar compositions found in Karelia. Aluminosilicate rocks are used as a fluxing component in glaze and enamel compositions and as the alumina and partly the alkali component in glass batches for special and general purpose glass.

Based on a study of feldspar rocks in Karelia, three genetic groups were distinguished that are the most interesting for the glass industry: pegmatite (Chupinskii and Priladozhskii groups of deposits), acid vulcanite (halleflinta from the Kostomukshskoe deposit, quartz porphyry from Roza-Lampi), and alkaline and nepheline syenite (Elet'ozerskii and Elisenvaarskii massifs).

The present study considers the effect of the chemico-mineralogical composition of aluminosilicate rocks on the properties and structure of low-melting engineering glasses. Comparative studies of glasses based on traditional industrial materials (pegmatite and nepheline syenite) and nontraditional materials (halleflinta and glasses made of pure chemical reactants) were carried out. The system selected for the study was $SiO_2 – Al_2O_3 – Na_2O (K_2O) – B_2O_3$, whose composition content was within the following limits (here and elsewhere wt.%): 10 – 25 Na_2O, 45 – 65 SiO_2, 4 – 12 Al_2O_3, 10 – 25 B_2O_3.

Technical glasses are complex heterogeneous systems consisting of oxides similar to the natural aluminosilicates but existing in slightly different ratios. The main components (SiO_2, Al_2O_3, Na_2O, K_2O, MgO, Fe_2O_3) are fully or partly introduced into these glasses via aluminosilicate rocks capable of forming glass in melting. The use of different aluminosilicate rocks in technical glass, especially in large quantities, can result in perceptible differences between the glass melts, despite their similar composition. Therefore, the production of glass based on natural aluminosilicate is related to a number of physicochemical factors, including the following:

– the special role of the components comprising the system; their possible coordination state and its effect on the process parameters and the properties of glass or materials based on this glass are analyzed;

– the relative resistance of the crystalline structure of aluminosilicate at normal temperatures of production of glass melts and the related phenomenon of the "crystallization memory"; visual physical heterogeneity of the melt does not mean its chemical and structural homogeneity, which has a perceptible effect on the viscosity and crystallization capacity of the glass melt [1].

– the chemico-mineralogical composition of natural material and the ratio of the components introduced as additives.

Three series of multicomponent glasses were melted using aluminosilicate materials (pegmatite, nepheline syenite, halleflinta) and chemically pure components (alumina, quartz, soda ash and borax). The chemical compositions of the feldspar materials are listed in Table 1. The series were composed in such a way that the glasses either contained equimolecular quantities of the components being compared or a successively varying quantity of one component, whereas the ratio between the other components remained constant.

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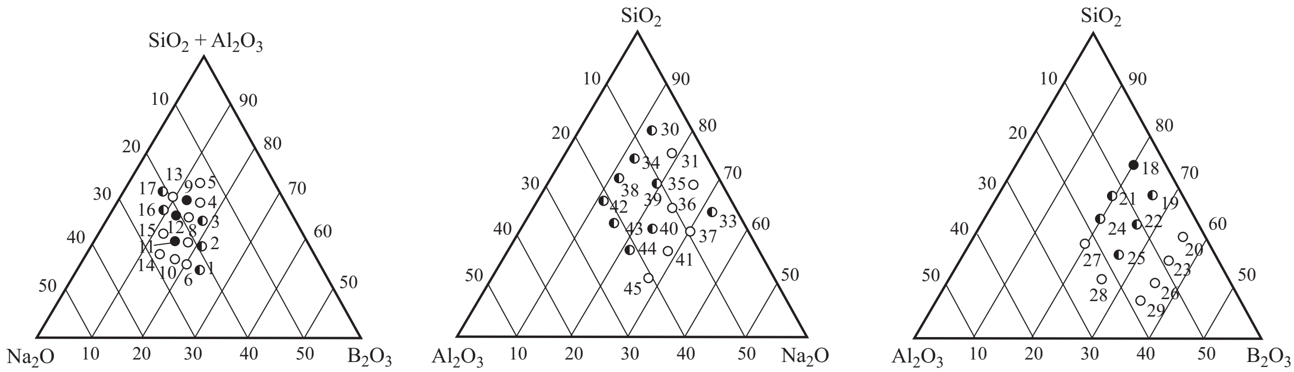

Fig. 1. Glass-formation regions in glasses based on natural aluminosilicates: ○) clear; ◐) nonclarified; ●) opalescent.

The batch was calculated taking into account the chemical compositions of the natural aluminosilicates. The glasses were melted in corundum crucibles in a silite furnace. The glass-melting temperature was 1250 – 1350°C with a 1-h exposure at this temperature. Annealing of glasses was carried out at 600 – 650°C. The effect of the components on the properties and structure of glasses was studied taking into account such properties as fusibility, TCLE, and acid resistance. The fusibility was determined from the spreadability of a cylindrical sample compressed from finely milled glass (particle size 0.063 mm) placed on a sloping surface and exposed for 4 min at 860°C. The acid resistance was determined according to GOST 10134.2–82 and GOST 24788–81. The TCLE was measured on a DKV-4 dilatometer within a temperature interval of 20 – 400°C.

The glass-forming ranges of the synthesized technical glasses based on natural aluminosilicates are shown in Fig. 1.

For theoretical substantiation of the development of low-melting technical glass based on natural aluminosilicates, the effect of Al_2O_3, B_2O_3, Na_2O, and SiO_2 on the properties and structure of glass was investigated. The main attention was paid to the modification of properties (spreadability, TCLE, acid resistance) occurring as a consequence of substitution of Al_2O_3 for SiO_2 in the presence of different constant quantities of B_2O_3 and Na_2O and substitution of SiO_2 for Na_2O and B_2O_3 in the presence of different constant quantities of Al_2O_3. For this purpose, the Al_2O_3 content in the first series of synthesized glasses varied from 4 to 12%. It was established that Al_2O_3 decreases the capacity of technical glass for spontaneous crystallization (Fig. 1).

The effect of Al_2O_3 introduced via various aluminosilicates on the spreadability, the TCLE, and the acid resistance of glasses is shown in Fig. 2. The curve shapes indicate that glasses based on halleflinta and nepheline syenite are lower-melting than glasses based on pegmatite and chemical reactants. Substitution of 4 to 12% Al_2O_3 for SiO_2 insignificantly increases the fusibility of glasses based on natural aluminosilicates, as in glasses based on pure chemical reactants. However, the spreadability results point to a different nature of glass melting, in spite of their identical composition.

It is known that the mineral structure plays a great role in the formation of the glass structure [2]. Aluminum plays a special role in the structure of natural aluminosilicates, as in silicate glasses. Aluminum in the melting of aluminosilicate can exist in different structural coordinations and has an effect on the glass melt properties. Being in the tetrahedral position, aluminum isomorphically replaces silicon; octahedral aluminum is an analog of Fe^{3+}, Mg^{2+}, and other metals [3].

Glasses based on nepheline syenite are lower-melting that glasses of other compositions, which is corroborated by their TCLE. Glasses based on halleflinta in the presence of constant quantities of Al_2O_3 are more fusible than glass based on pegmatite and chemical reactants. A distinctive feature of halleflinta is its finely disperse structure and the eutectic ratio of quartz to albite, which contributes to the fusibility of glasses [1].

Modification of the TCLE and acid resistance in glasses depending on the Al_2O_3 content has an effect on the glass structure. This is substantiated by the anomalies on the curves with a 6% Al_2O_3 content. When the quantity of alumi-

TABLE 1

Material	Weight content, %							
	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	calcination loss
Pegmatite	76.95	13.00	0.84	0.60	3.55	3.88	0.69	0.52
Nepheline syenite	42.10	25.90	1.89	0.96	8.10	15.30	3.70	1.10
Halleflinta	70.22	17.79	2.03	0.65	1.07	6.25	0.88	0.64

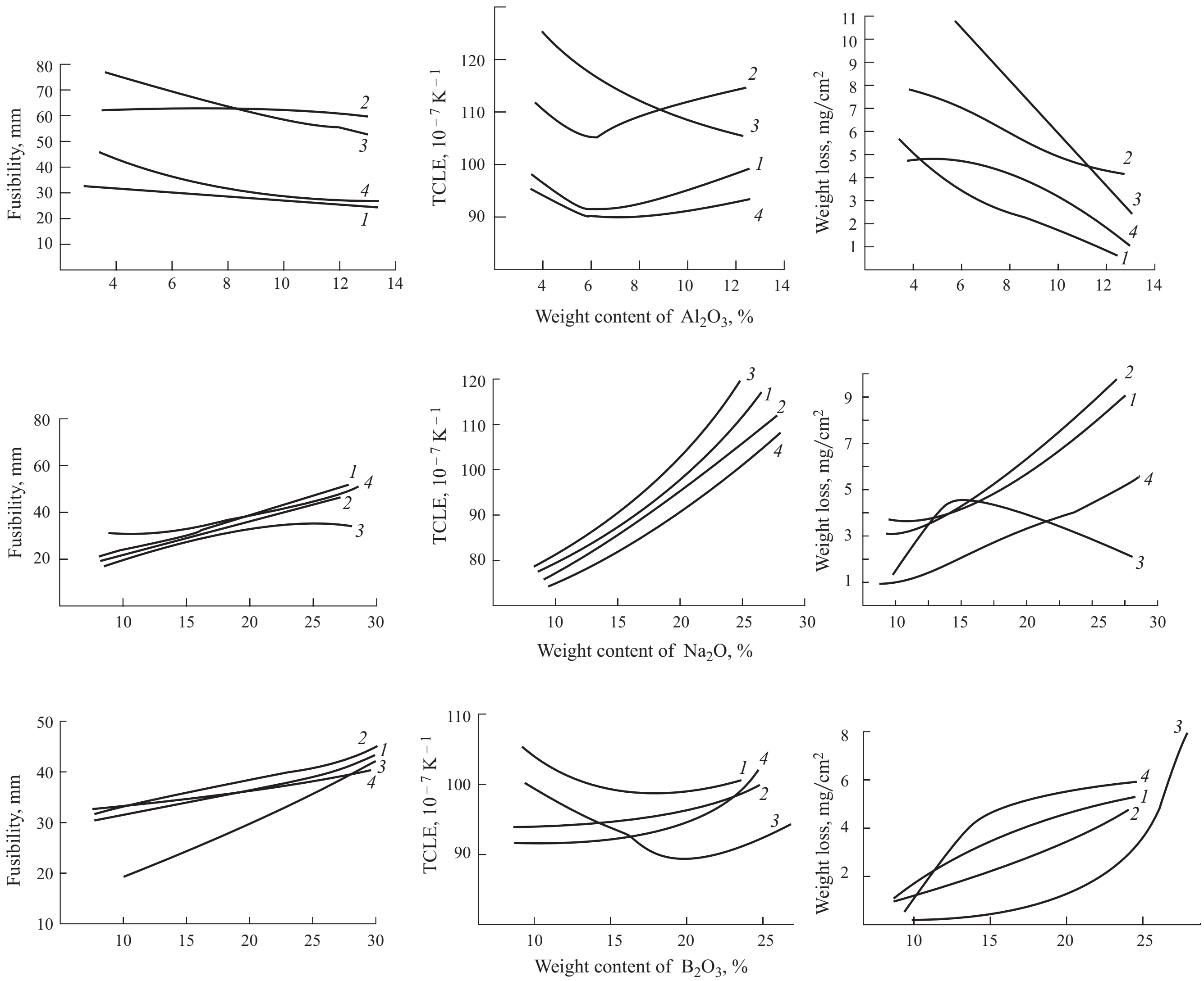

Fig. 2. The effect of Al_2O_3, Na_2O, and B_2O_3 on the fusibility, TCLE, and acid resistance of glasses based on pegmatite (*1*), nepheline syenite (*2*), halleflinta (*3*), and chemical reactants (*4*).

num is insignificant (4%), the TCLE of the glass decreases, and when the quantity of Al_2O_3 introduced reaches 6% and more, the TCLE of the glasses grows. According to the data in [1], a break in the TCLE curve can be considered a consequence of the oxygen ion breaking away from the alkaline oxides to form [AlO_4] tetrahedra. The acid resistance of glasses grows with increasing aluminum content; however, these characteristics in glasses differ, which is presumably related to the structural patterns and to the chemico-mineralogical composition of natural aluminosilicates.

The second series of glasses was used to study the effect of alkali oxides on glass formation and glass properties (Fig. 2). Alkaline oxides are present in aluminosilicates (nepheline $KNa_3[AlSiO_4]_4$, albite $Na[AlSi_3O_8]$, and orthoclase $K[AlSi_3O_8]$) in different amounts and their content varies within the limits of $K_2O : Na_2O = 0.2 – 2.0$ (Table 1). The alkali ratio determines the application area of glasses; however, in most practical cases the main factor is the sum of the alkali oxides ($K_2O + Na_2O$), which should be at least 7% (GOST 13451–77). Although alkali metal oxides have a significant effect on the glass properties, it should be noted that, as a consequence of the complication of the composition, the properties of the alkaline oxides, which clearly depend on the radius of K^+ and Na^+ ions in binary systems, become significantly modified. According to the data in [2], the chemical resistance of borosilicate glasses grows when using alkali cations with different ionic radii. Partial replacement of Na_2O by K_2O in sodium-titanium-borosilicate enamels intensifies their opacification and increases their fusibility. The presence of more than 9% K_2O in the a glass composition decreases its spreadability [3].

The effect of Na_2O on the crystallization capacity of experimental glasses is shown in Fig. 1. The glass-formation range in glasses based on natural aluminosilicates is shifted

to an increasing Na_2O content from 10 to 25%. The crystallization capacity of technical glasses increases with a low content of alkalis (10%) and aluminum oxide (4%) and causes opalescence, compared to glasses based on chemical reactants. Glasses based on nepheline syenite even with a high quantity of alkalis (20 – 25%) do not become clarified due to the high content of ferric oxide in the structural lattice of the aluminosilicate.

In studying aluminosilicates with a different content of alkaline oxides, a decreased fusibility of glasses based on halleflinta was registered in glasses of the second series, in spite of the fact that other compositions had the same content of alkali oxides and aluminum oxide. As the content of Na_2O in glasses based on natural aluminosilicates grows from 10 to 25%, the TCLE perceptibly grows but the acid resistance decreases. It is worth noting that glasses based on pegmatite are lower-melting than other composition of glasses. The TCLE of glasses based on chemical reactants varies insignificantly $(83 - 87) \times 10^{-7}\ K^{-1}$ compared with glasses based on natural aluminosilicates $(82 - 104) \times 10^{-7}\ K^{-1}$. Although it is generally accepted that the acid resistance of silicate glasses decreases with an increasing quantity of alkalis, the acid resistance in glasses based on aluminosilicates does not always depend directly on the Na_2O content and can even grow with it (Fig. 2).

The B_2O_3 content in glasses of the third series varied from 10 to 25%. Boric anhydride effectively lowers the tendency of technical glass for spontaneous crystallization (Fig. 1). B_2O_3 additives make it possible to obtain low-melting glazes and enamels without a risk of their crystallization during firing of the products. A variation of the B_2O_3 content from 10 to 25% is accompanied by increasing fusibility of the glasses (Fig. 2). Glasses with 6% Al_2O_3 are distinguished by a minimum in the curve with a B_2O_3 content equal to 16%.

A comparison of the TCLE of glasses reveals their differences depending on the natural aluminosilicate used. As the B_2O_3 content increases to 18%, the TCLE of the glasses decreases and then increases. Boric anhydride has a different effect on the acid resistance of silicate glasses depending on its content and its coordination state [2]. The presence of a minimum on the curve of the halleflinta-based glass can be accounted for by a change in the coordination state of boron in the melt. The $[BO_4]$ tetrahedra facilitate consolidation of the glass skeleton and increase its chemical resistance [2]. The acid resistance of experimental glasses decreases as the content of boric anhydride increases. Glasses based on halleflinta with small quantities of B_2O_3 have a higher acid resistance (10%) than glasses based on chemical reactants, nepheline concentrate, and pegmatite.

Thus, the mineralogical composition and structure of natural aluminosilicate materials, as well as the ratio of $Na_2O : B_2O_3$ additives, have an effect on the physico-technological properties of engineering glass. The use of various natural aluminosilicates in such glasses does not significantly disturb the glass-forming conditions and does not require an elevated melting temperature but makes it necessary to correct the ratios between the main components and additives.

Compositions for engineering glasses have been developed on the basis of natural aluminosilicates from Karelia [4], including tinted opacified glasses used in construction, undercoat, and tinted cover glass enamels for metals, and low-melting glazes for ceramics.

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